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Oxidative doping of α,ω -dithienylpolyenes : bipolaron destabilization by electron withdrawing groups

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NORTHERN ILLINOIS UNIVERSITY

OXIDATIVE DOPING OF α,ω -DIPHENYLPOLYENES: BIPOLARON
DESTABILIZATION BY ELECTRON WITHDRAWING GROUPS

A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
BACHELOR OF SCIENCE WITH HONORS

BY

BRADLEY D. GATES

JANUARY, 1988

APPROVAL SHEET

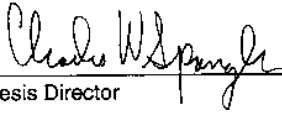
Title of Thesis: Oxidative Doping of α,ω -Diphenylpolyenes: Bipolaron
Destabilization by Electron Withdrawing Groups

Name of Candidate: Bradley D. Gates
Bachelor of Science (Honors in Chemistry)
January, 1988


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Certification: In accordance with departmental policies, this thesis is
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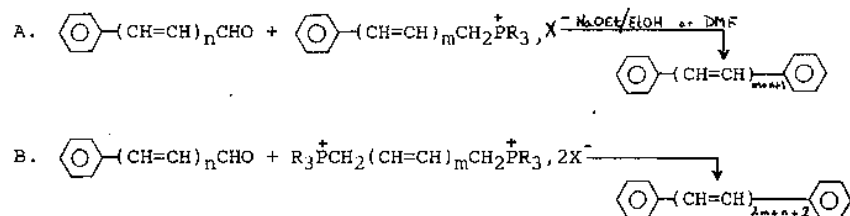
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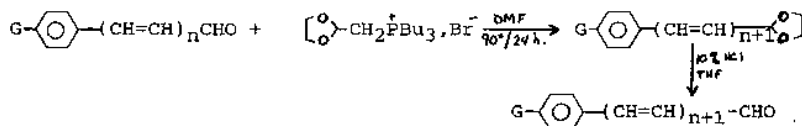
Introduction:

The discovery that the electrical conductivity of polyacetylene could be increased dramatically upon oxidative or reductive "doping" with iodine or AsF_5 caused a rapid growth in the conducting polymer field that is still ongoing today. One of the biggest problems a chemist studying conducting polymers faces is the insolubility of the materials being studied. Much work has been done, therefore, to develop soluble polymer precursors or oligomers to serve as models for conducting polymers. Current studies in our laboratory have involved the synthesis and the oxidative doping of one such system, namely α,ω -diphenylpolyenes. These types of compounds are attractive to the organic chemist because they can be made from relatively simple and inexpensive materials in fairly high yields. The synthesis involves reacting a conjugated aromatic polyenal in a typical Wittig reaction with either mono or bisphosphoranes as shown below in Scheme 1. Aromatic polyenals can be obtained by a process developed



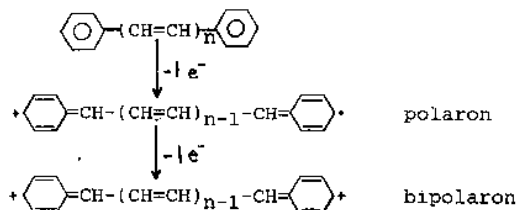
Scheme 1. Formation of α,ω Diphenylpolyenes by Wittig Condensation

by Crespi¹; however, this reaction has been dramatically improved by Spangler and McCoy² as shown in Scheme 2.



Scheme 2. Extension of Polyenals
G= EDG or EWG

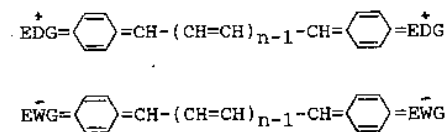
Conduction in the doped α,ω -diphenylpolyenes is governed by consecutive one-electron transfers first forming radical anions or cations (polarons) and then dianions or dications (bipolarons). In the case of oxidative doping agents, the polyene is sequentially oxidized to a polaron and then bipolaron states, as shown in Scheme 3. The conjugated system



Scheme 3. Oxidative Doping of Diphenyl Polyenes

distorts around the resulting positive charge by switching the positions of the carbon-carbon double and single bonds forming the polaron. The bipolaron can then be formed with

the removal of a second electron. The formation of the polaron and bipolaron can be observed in solution by UV-Vis absorption spectroscopy as described by Spangler et al³. The doped species gives rise to two new bands in the mid-gap that are at much lower energy than the original $\pi \rightarrow \pi^*$ transition of the undoped polyene. One would predict that by increasing the conjugation length, the mid-gap transition energy would continually decrease due to increased delocalization and stabilization. Recent studies in collaboration with Dalton's group at the University of Southern California⁴ have confirmed Spangler's interpretation of the UV-Vis absorption spectra upon doping and have shown that the new species attributed to polaron formation is paramagnetic, while the more stable species is diamagnetic. One could also predict that electron donating groups (EDG) or electron withdrawing groups (EWG) substituted at the para position of the phenyl rings would have the effect of stabilizing or destabilizing the bipolaron depending upon the nature of the charged states as shown in Scheme 4.



Scheme 4. Predicted Stabilization of Bipolaron States by Electron Donating or Withdrawing Groups

Results and Discussion

The Cresp method for extending conjugation in polyenals by Wittig oxypropenylation was found to be unsuccessful for extending phenylpolyenals containing electron donating groups. Substitution of $(n\text{-Bu})_3\text{P}$ for $(\text{C}_6\text{H}_5)_3\text{P}$ in the Wittig salt increases the yield of the process, and allows one to extend phenyl groups that are substituted with EDGs or EWGs². Once the desired extended aldehyde is obtained, Wittig condensation can be accomplished utilizing bisphosphoranes to yield bis-substituted polyenes. These reactions were carried out over the past two years by several workers in our group⁵ and the results are summarized in Table 1.

Doping studies were carried out in dilute solution (10^{-5} M) in methylene chloride and the dopant (SbCl_5) was added in aliquot amounts as a CH_2Cl_2 solution. In all cases, excess dopant was utilized (100x) to insure rapid and complete polaron and bipolaron formation. The bipolaron products are stable in solution for several hours and their formation and decay can be followed easily using a Varian 2290 UV-visible spectrophotometer.

If polarons and bipolarons are indeed formed upon oxidative doping, then electron-withdrawing groups should destabilize the dication state. In addition, the degree of oxidation as evidenced by a slower rate of intermediate formation or reduced molar absorptivity, should be observable when compared to the spectra of the unsubstituted parent structures as reported by Spangler et al³. The results of

these studies are shown in Table 2.

In all cases except for Cl, electron-withdrawing groups suppress bipolaron formation in the pentaene series compared to the parent. Bipolaron formation is found in the hexaene series, but with reduced molar absorptivities and at a higher transition energy than the parent. This conforms very well with the predicted behavior. Chlorine represents a unique exception because it is electron withdrawing via an inductive effect, but is an electron donating group via resonance stabilization. Since bipolaron stabilization depends heavily upon the resonance effect, we see that chlorine does stabilize the bipolaron state slightly when compared to the parent pentaene and hexaene.

One finds, as predicted, that destabilization of the polaron and bipolaron occurs when electron withdrawing groups are placed at the para position of the rings. One also finds that the amount of destabilization is dependent on the strength of electron withdrawing character the substituent possesses. However, when groups such as chlorine are used, resonance stabilization outweighs inductive electron withdrawal.

Experimental

All UV spectra were recorded with a Varian 2290 spectrophotometer. ^1H NMR spectra were determined as solutions in CDCl_3 using an IBM 200 MHz spectrometer.

For the UV spectra and doping studies, all solutions

were 10^{-5} M in CH_2Cl_2 . The spectrum of the undoped polyene was recorded from 900-230 nm. The solutions were then doped with approximately a 100-fold excess of SbCl_5 (10^{-2} M in CH_2Cl_2). Initially, the SbCl_5 was added directly to the cuvette using a microsyringe, but the SbCl_5 rapidly hydrolyzed in the air and tended to clog the tip of the syringe. To alleviate this problem, the dopant was added to the cuvette dropwise using a Pasteur pipette. The UV spectrum of the doped species was taken immediately after doping and then repeated 10-15 minutes after doping.

3-(4'-cyanophenyl)-2-propenal-- A solution of sodium ethoxide (150 ml, 1 M soln) in absolute ethanol was added dropwise to a solution of p-cyanobenzaldehyde (13.1 g, 0.1 mole) and 1,3-dioxan-2-ylmethyltributylphosphonium bromide (0.11 mole, 92 ml, 1 M soln) in 250 ml DMF. The resulting solution was stirred at room temperature overnight (16-20 h.), after which, it was poured into 1 L of water. The product was extracted with ether (3 x 300 ml), washed with saturated NaCl solution (3 x 200 ml), and dried over MgSO_4 . After filtration and removal of the ether by rotovap, the residue was dissolved in THF (250 ml). A 10% aqueous solution of HCl was added (250 ml), and the mixture was stirred at room temperature for 2 h., after which it was poured into 1 L of water, extracted and washed as before. After filtration and removal of solvent, the solid was recrystallized from DMF/toluene, yielding 3-(4'-cyanophenyl)-2-propenal (8.0 g,

51%), m.p. 131-133°C, $^1\text{H NMR}$ (CDCl_3): δ 6.8 (dd $J=7.2, 14.9$ Hz), δ 7.5 (d $J=13.7$ Hz), δ 7.7 (q $J=$ δ 9.75 (d $J= 7.2$ Hz).

3-(4'-trifluoromethylphenyl)-2-propenal-- A solution of sodium ethoxide (150 ml, 1 M soln) in absolute ethanol was added dropwise to a solution of p-trifluoromethylbenzaldehyde (8.7 g, 0.05 mole) and 1,3-dioxan-2-ylmethyltributylphosphonium bromide (52ml, 1.2 M soln, 0.062 mole) in 200 ml DMF. The resulting solution was stirred at room temperature overnight, after which it was poured into 1 L water. The product was extracted in ether (3 x 300 ml), washed with saturated NaCl solution (2 x 200 ml), and dried over MgSO_4 . After filtration, ether was removed by rotovap and the residue was dissolved in 250 ml THF. A 10% aqueous HCl solution (250 ml) was added, and the resulting mixture was stirred at room temperature for 2 h., after which it was poured into 1L water, extracted, and washed as before. After filtration and removal of solvent, the residue was dissolved in a minimal quantity of ethyl acetate and chromatographed over silica, eluting with 20% EtOAc/hexane. Chromatography yielded essentially pure 3-(4'-trifluoromethylphenyl)-2-propenal (9.0 g, 90%), m.p. dec , $^1\text{H NMR}$ (CDCl_3): δ 6.8 (dd $J=17.9, 7.2$ Hz), δ 7.55 (d $J=14.9$ Hz), δ 7.7 (s ArH) δ 9.75 (d $J= 7.2$ Hz).

General pentaene preparation

An 50% excess of 1 M sodium ethoxide solution is added

dropwise to a solution of the aldehyde (0.025 mole) and 2 buten 1,4-bis(tributyl)phosphonium bromide (20 ml, 0.5 M soln, 0.01 mole). The resulting solution is stirred overnight at room temperature and then vacuum filtered. The solid is recrystallized from a suitable solvent (in most cases toluene DMF or pure DMF).

1,10-(4,4'-bis-cyanophenyl)-deca-1,3,5,7,9-pentaene- The product was prepared from p-cyanocinnamaldehyde (4.0 g, 0.025 mole) and a solution of the Wittig salt (20 ml, 0.5M soln) by the general procedure (2.17 g, 63%), m.p. 190° (d)

1,10(4,4'-bis-trifluoromethylphenyl)-deca-1,3,5,7,9-pentaene was prepared from p-trifluoromethylcinnamaldehyde by the general procedure (3.15 g, 30%) m.p. 220-221°.

General hexaene procedure

An excess of 1 M sodium ethoxide is added dropwise to a solution of the aldehyde (0.025 mole) and 2,4-hexadien-1,6-bis(tributyl)phosphonium bromide (0.01 mole) in ethanol. The solution is stirred at room temperature overnight and vacuum filtered. The solid is then recrystallized from a suitable solvent (DMF/toluene or pure DMF).

1,12-(4,4'-bis-cyanophenyl)-dodeca-1,3,5,7,9,11-hexaene was prepared from p-cyanocinnamaldehyde by the general procedure (1.05 g, 30%), m.p. 262-4° (d)

1,12(4,4'-bis-trifluoromethylphenyl)-dodeca-1,3,5,7,9,11-hexaene was prepared from p-trifluoromethylcinnamaldehyde by the general procedure (2.79 g, 25%), m.p. 236-8° (d)

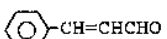
Acknowledgment

I would like to thank Dr. Spangler for all his help and patience with all of my research endeavors during my last few years at NIU.

<u>Aldehyde</u>	<u>Bisphosphorane</u>	<u>Product</u>	<u>Yield(%)</u>
O ₂ N-R	A	O ₂ N-R'-NO ₂ (n=5)	64
O ₂ N-R	B	O ₂ N-R'-NO ₂ (n=6)	42
Cl-R	A	Cl-R'-Cl (n=5)	43
Cl-R	B	Cl-R'-Cl (n=6)	36
NC-R	A	NC-R'-CN (n=5)	63
NC-R	B	NC-R'-CN (n=6)	30
F ₃ C-R	A	F ₃ C-R'-CF ₃ (n=5)	30
F ₃ C-R	B	F ₃ C-R'-CF ₃ (n=6)	25

A = Bu₃P=CHCH=CHCH=PBu₃

B = Bu₃P=CH(CH=CH)₂CH=PBu₃

R = 

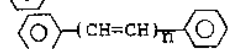
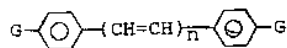
R' = 

Table 1. Preparation of 4-EWG-Phenyl-4'-EWG-Phenyl Polyenes

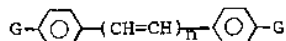


G	n	Bipolaron Absorption Maxima (nm)
H	5	612, 564
H	6	673, 618
CF ₃	5	bipolaron not observed ^a
CF ₃	6	650, 602
Cl	5	630, 580
Cl	6	690, 635
CN	5	550, 605 ^b
CN	6	654, 595
NO ₂	5	bipolaron not observed ^a
NO ₂	6	653, 604

a No bipolaron peak observed, but a weak peak at approx. 700 nm formed in addition to polyene $\pi \rightarrow \pi^*$ decay

b Very weak absorption, wavelength assignment ± 5 nm

Table 2. Bipolaron Spectra of Doped 4-EWG-Phenyl-4'-EWG-Phenyl Polyenes



G	n	λ_{max} , nm ($\epsilon_{\text{max}} \times 10^{-3}$)
CF ₃	5	364(sh), 383(10.1), 403(15.3), 429(13.4)
CF ₃	6	379(sh), 400(8.0), 422(12.5), 449(11.4)
Cl	5	363(sh), 384(7.7), 405(11.6), 441(10.2)
Cl	6	379(sh), 395(4.3), 421(6.4), 449(5.7)
CN	5	376(sh), 395(6.5), 419(9.2), 445(7.7)
CN	6	386(sh), 413(6.2), 435(8.8), 463(7.5)
NO ₂	5	450(5.9)
NO ₂	6	465(9.2)

Table 3. Absorption Spectra of Undoped 4-EWG-Phenyl-4'-EWG-Phenyl Polyenes

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